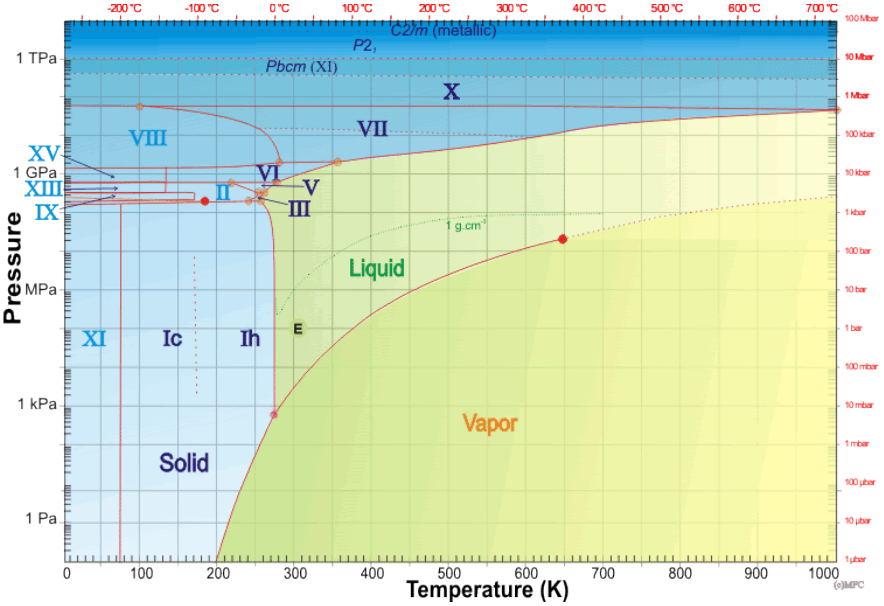
Water Phase Diagram

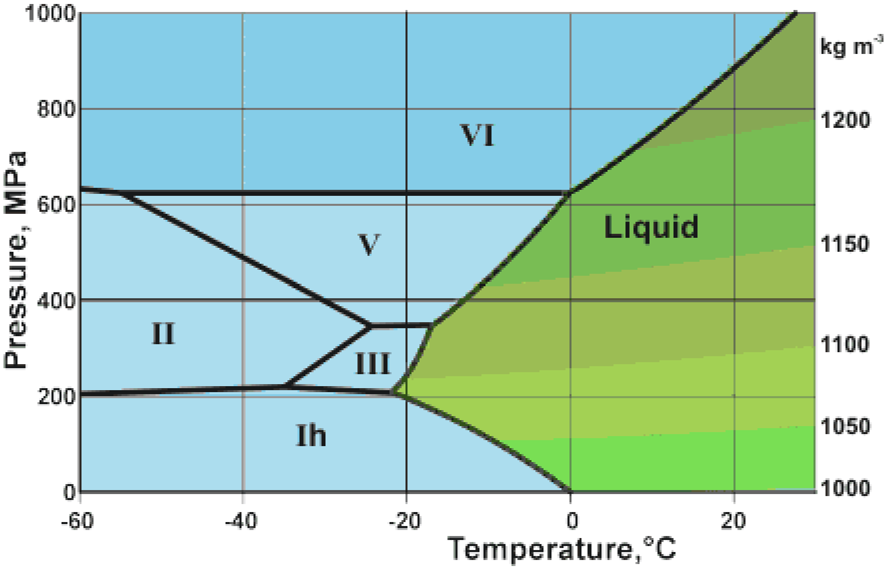
Phase diagrams

Phase diagrams show the preferred physical states of matter at different temperatures and pressure. Within each phase, the material is uniform with respect to its chemical composition and physical state. At typical temperatures and pressures on Earth (marked by an '**E**' below) water is a liquid, but it becomes solid (that is, ice) if its temperature is lowered below 273 K and gaseous (that is, water vapor)[a] if its temperature is raised above 373 K, at the same pressure. Each line (phase line)[e]on a phase diagram represents a phase boundary and gives the conditions when two phases may stably coexist in any relative proportions (having the same Gibbs free energy). Here, a slight change in temperature or pressure may cause the phases to abruptly change from one physical state to the other. Where three phase lines join, there is a 'triple point', when three phases stably coexist (having identical Gibbs free energies),[e] but may abruptly and totally change into each other given a slight change in temperature or pressure. Under the singular conditions of temperature and pressure where liquid water, gaseous water and hexagonal ice stably coexist, there is a 'triple point' where both the boiling point of water and melting point of ice are equal. Four phase lines cannot meet at a single point. A 'critical point' occurs at the end of a phase line where the properties of the two phases become indistinguishable from each other, for example when, under singular conditions of temperature and pressure, liquid water is hot enough and gaseous water is under sufficient pressure that their densities are identical. Critical points are usually found at the high temperature end of the liquid-gas phase line.

The phase diagram of water

The phase diagram of water is complex,[b ,f] having a number of triple points and one, or possibly two, critical points. Many of the crystalline forms may remain metastable in much of the low-temperature phase space at lower pressures. A thermodynamic model of water and ices Ih, III, V and VI [1320] and thermodynamic functions of the phase transitions [1658] have been described. The known ices can be divided, by cluster analysis of their structures [1717], into the low-pressure ices (hexagonal ice, cubic ice and ice-eleven). the high pressure ices (ice-seven, ice-eight and ice-ten) and the others (found in the relatively narrow range of moderate pressures between about 200-2000 MPa). All phases that share phase boundaries with liquid water (ices Ih, III, V and VI and VII) have disordered hydrogen bonding. The phases with ordered hydrogen bonding are found at lower temperatures and are indicated in light blue below. The structural transformation conditions of some of these ices during compression have been described [1795] .





Mouse over border for D_2O phase lines

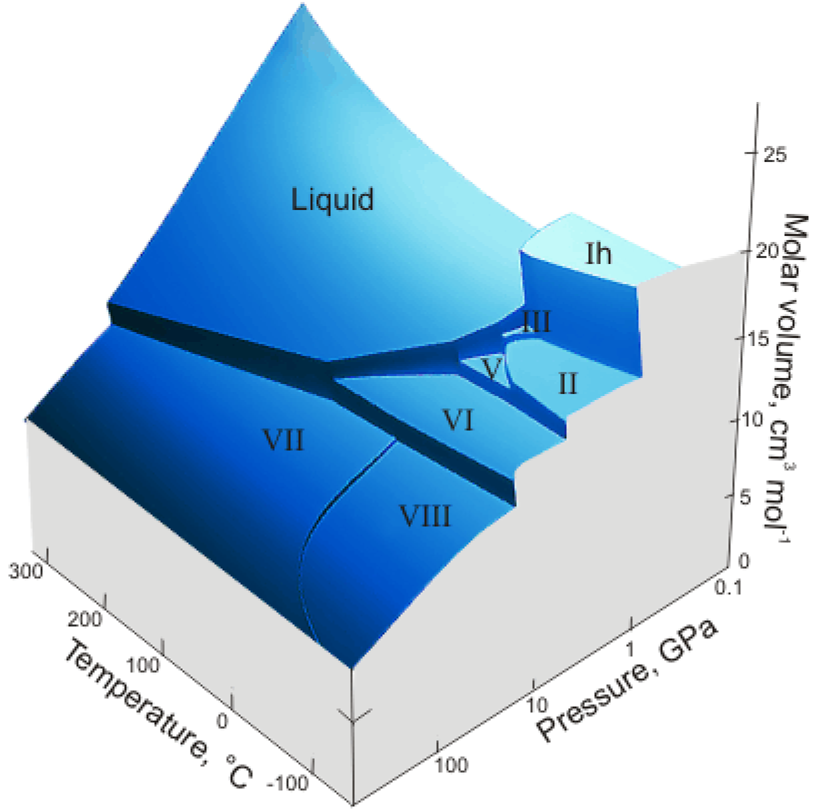
The mean surface conditions on **E**arth, (also atmospheric conditions, **M**ars and **V**enus on mousing over Earth) are indicated. The complex central part of the phase diagram is expanded opposite. The critical point and the orange line in the ice-one phase space refer to the low-density (LDA) and high-density (HDA) forms of amorphous water (ice) [16]. Although generally accepted and supported by diverse experimental evidence [754a, 861], the existence of this second, if metastable, critical point is impossible to prove absolutely at the present time and isdisputed by some [200, 618, 628, 754b, 1115]. The transition between LDA and HDA is due to the increased entropy and attractive van der Waals contacts in HDA compensating for the reduced strength of its hydrogen bonding.

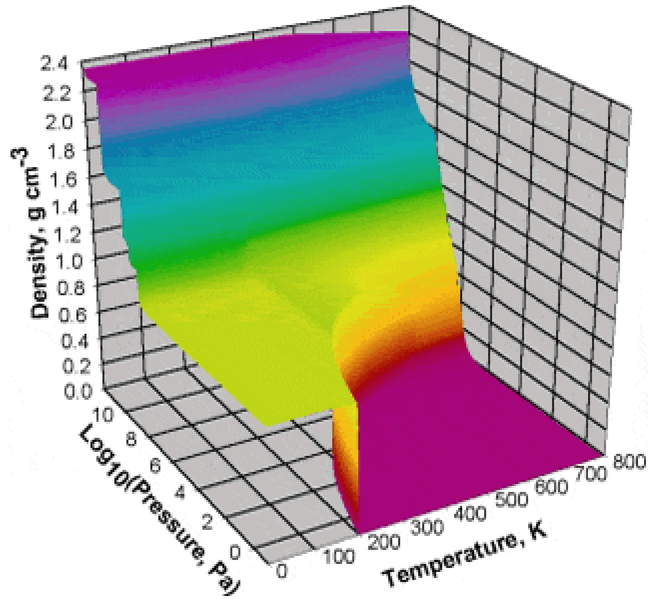
The high-pressure phase line between ice-ten (X) and ice-eleven (XI) [81] is still subject to experimental verification. The melting point line between supercritical water and high pressure ice has been established [691, 2096]. Ice VII possesseshigher and lower pressure forms [1428]. A phase diagram of water at higher temperatures, up to 9000 K, has been proposed [1671].

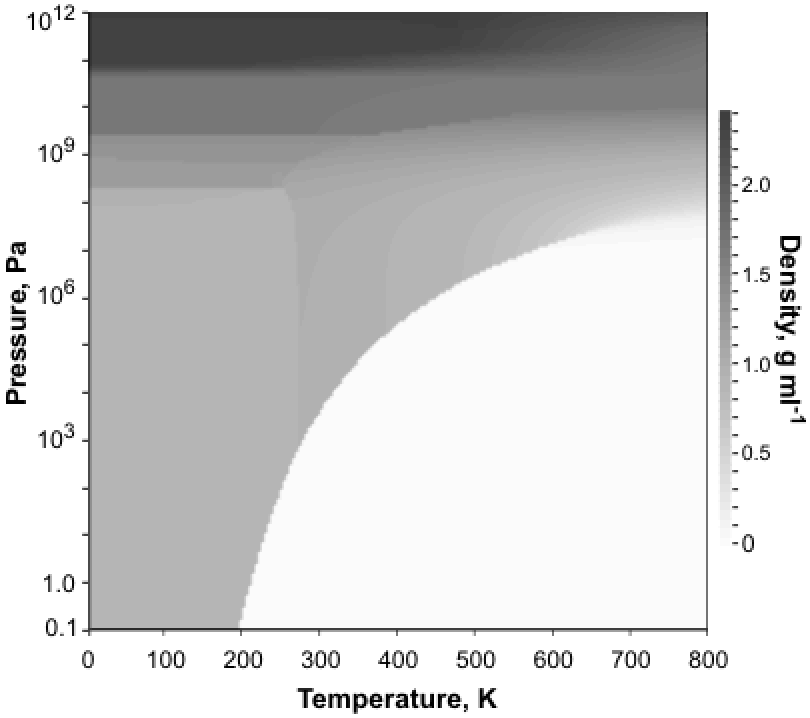
Both the critical points are shown as red circles in the phase diagram, above. Beyond the critical point in the liquid-vapor space (towards the top right, above), water is supercritical existing as small but liquid-like hydrogen-bonded clusters dispersed within a gas-like phase [456, 894, 1962], where physical properties, such as gas-like or liquid-like behavior, vary in response to changing density and the normal distinction between gas and liquid has disappeared [1766] . The critical isochor (density 322 kg m^{-3}) is shown as the thin dashed line extension; this may be thought of as dividing more-liquid-like and more-gas-like properties [540].[d] The properties of supercritical water[c] are very different from ambient water. For example, supercritical water is a poor solvent for electrolytes, which tend to form ion pairs. However, it is such an excellent solvent for non-polar molecules, due to its low dielectric constant and poor hydrogen bonding, that many are completely miscible. Viscosity and dielectric both decrease substantially whereas auto-dissociation increases substantially. The physical properties of water close to the critical point (near-critical) are particularly strongly affected [677], Extreme density fluctuations around the critical point causes opalescent turbidity. Many properties of cold liquid water change above about 200 MPa (for example, viscosity, self-diffusion, compressibility, Raman spectra and molecular separation), which may be explained by the presence of a high density liquid phase containing interpenetrating hydrogen bonds. The chemical properties of water are also greatly changed at high temperatures and pressures due to the changes in dissociation,solubility, diffusivity and reactivity due to decreasing hydrogen-bonding [1116]. [**Back to Top** ▲]

Density changes

As pressure increases, the ice phases become denser. They achieve this by initially bending bonds, forming tighter ring or helical networks, and finally including greater amounts of network inter-penetration. This is particularly evident when comparing ice-five with the metastable ices (ice-four and ice-twelve) that may exist in its phase space.



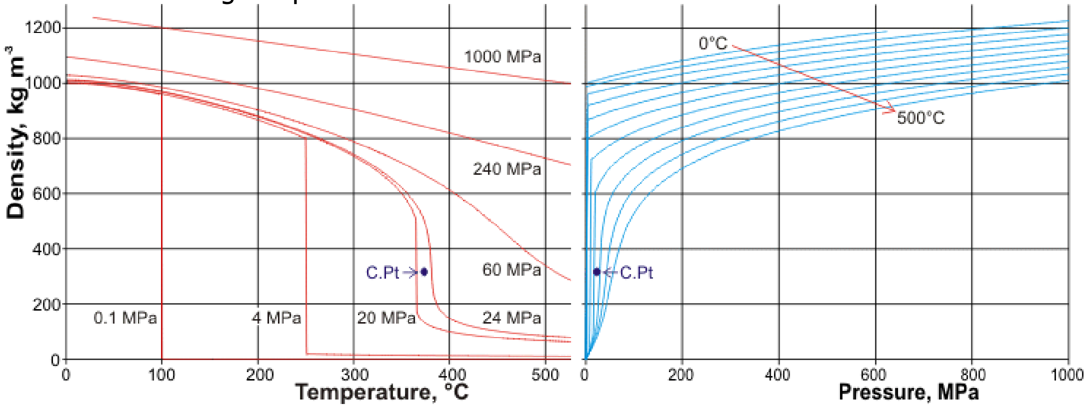


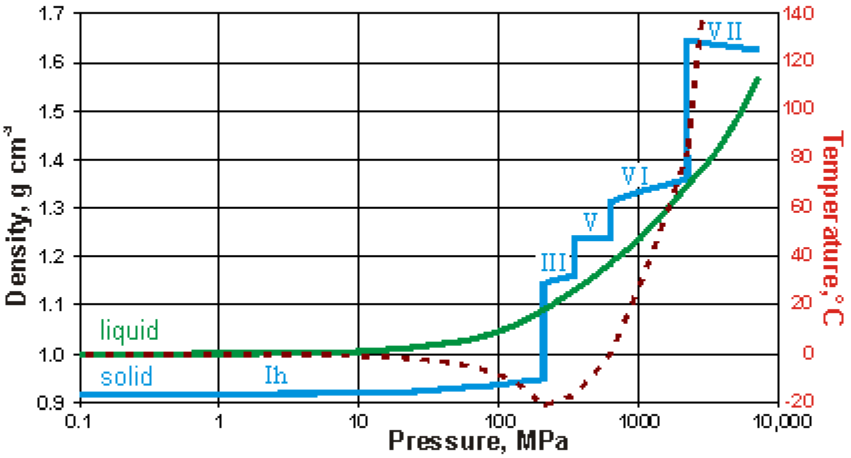


The liquid-vapor density data for the graphs above, opposite and below were obtained from the IAPWS-95equations [540].

Other phase diagrams for water are presented elsewhere [681]. The density of supercooled (emulsified) water under pressure has recently been determined [1685].

The two graphs below show the variation in the density of liquid, gaseous and supercritical water with temperature and pressure. The density of liquid water increases with increasing pressure and decreases with increasing temperature.





Seen opposite is the density of liquid and solid (that is the ices) water along the liquid-solid phase line. Note that temperature varies along this phase line (as shown dashed red). Hexagonal ice is less dense than liquid water whereas the other ices found in equilibrium with water are all denser with phase changes occurring on the approach of the liquid and solid densities.

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Triple points

Triple points occur where three phase lines join and the three phases may coexist at equilibrium.

Thermodynamic data for the triple points of water

Triple points			**MPa**	**°C**	**ΔH, kJ mol^{-1}**	**ΔS, J mol^{-1} K^{-1}**	**ΔV cm^{3}mol^{-1}**	**Ref.**	**D_2O** [717]
gas	liquid	Ih	0.000611657	0.010				536	661 Pa, 3.82 °C[70]
			gas→liquid		-44.9	-165	-22050	1833	
			gas→Ih		-50.9	-186	-22048		
			liquid→Ih		-5.98	-22	1.634		

gas	Ih	XI	0	-201.0				717	0 MPa, -197°C
liquid	Ih	III	209.9	-21.985				537	220 MPa, -18.8°C
			liquid→Ih		-4.23	-16.9	2.434	1833	
			liquid→III		-3.83	-15.3	-0.839		
			Ih→III		0.39	1.6	-3.273		
Ih	II	III	212.9	-34.7				537	225 MPa, -31.0°C
			Ih→II		-0.75	-3.2	-3.919	1833	
			Ih→III		0.17	0.7	-3.532		
			II→III		0.92	3.8	0.387		
II	III	V	344.3	-24.3				537	347 MPa, -21.5°C
			II→III		1.27	5.1	0.261	1833	
			II→V		1.20	4.8	-0.721		
			III→V		-0.07	-0.2	-0.982		
II	VI	XV						1582	~0.8 GPa, -143°C
liquid	III	V	350.1	-16.986				537	348 MPa, -14.5°C
			liquid→III		-4.61	-18.0	-0.434	1833	
			liquid→V		-4.69	-18.3	-1.419		
			III→V		-0.07	-0.2	-0.985		
liquid	IV	XII	~500-600	~-6				1300	
II	V	VI	~620	~-55				539	
liquid	V	VI	632.4	0.16				537	629 MPa, 2.4°C
			liquid→V		-5.27	-19.3	-0.949	1833	
			liquid→VI		-5.29	-19.4	-1.649		
			V→VI		-0.02	-0.5	-0.700		
VI	VIII	XV						1582	~1.5 GPa, -143°C
VI	VII	VIII	2,100	~5				8	1950 MPa, ~0°C
			VI→VII		-0.09	-o.3	-1.0	1833	
			VI→VIII		-1.20	-4.2	-1.0		
			VII→VIII		-1.10	-3.9	0.0		
liquid	VI	VII	2,216	81.85				537	2060 MPa, 78°C
			liquid→VI		-6.36	-18.0	-0.59	1833	
			liquid→VII		-6.36	-18.0	-1.64		
			VI→VII		0.0	0.0	-1.05		
VII	VIII	X	62,000	-173				538	
liquid	VII	X	43,000	>700				612a	
			47,000	~727				612b	
liquid	VII	Superionic	~40,000	~1000				1572	

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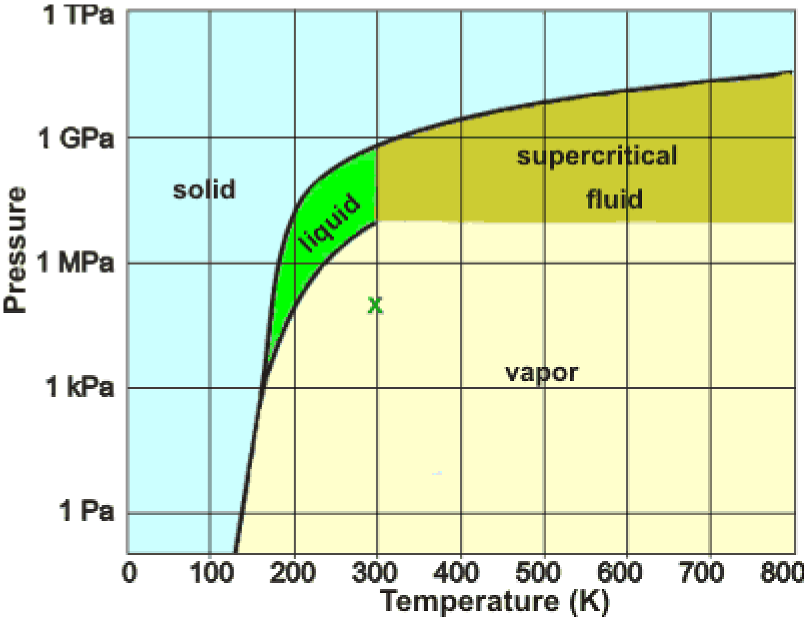
Footnotes

[a] Gaseous water is water vapor. In science and engineering, the word 'steam' is also used for water vapor, but usually when above the boiling point of water. As commonly used in the English language, 'steam' also may mean the white cloud of fine liquid water droplets of condensed water vapor that is produced by a boiling kettle, for example. Water is present in the atmosphere in both liquid and gaseous forms. For example, when we breathe out we expire an aerosol of fine (nm - µm+ radius) water droplets plus water vapor. This aerosol has been detected by a water-cluster-detecting breath sensor developed for detecting drunk or drowsy drivers [1801]. [Back]



[b] If water behaved more typically as a low molecular weight material, its phase diagram may have looked rather like this (where 'x' marks ambient conditions on earth). [Back]

[c] Supercritical water presents a reactive environment [1507]. Neutron diffraction has shown that tetrahedral liquid-like states are observed in supercritical water at above a threshold density, while below this threshold density gas-like water forms small, trigonal, sheet-like configurations [1508]. Under extreme conditions (e.g. 2.38 g cm^{-3}, 3000 K), dense hot water may be extremely reactive [1564]. [Back]

[d] This isochor is outwardly similar to the loci of the C_P maximum, and the thermal expansion and compressibility maxima, (the 'Widom' line [1715]). Above the line is a more 'liquid-like' material and below the line is a more 'gas-like' environment. However, the Widom lines for isobaric heat capacity, isochoric heat capacity, isothermal compressibility, isobaric thermal expansion, mass density and the molar internal energy all differ, particularly at higher pressures [1923]. A case has been put for a different line (the `Frenkel line') that separates liquid and gas-like fluids on their dynamic properties above the critical point [1961]. [Back]

[e] On a phase line the Gibbs free energies of the two phases (G_1, G_2) must be equal and remain equal if conditions change causing movement along the phase line. Thus

$$\left(\frac{\partial G_1}{\partial T}\right)_P dT + \left(\frac{\partial G_1}{\partial P}\right)_T dP = \left(\frac{\partial G_2}{\partial T}\right)_P dT + \left(\frac{\partial G_2}{\partial P}\right)_T dP$$

But, $\left(\frac{\partial G}{\partial T}\right)_P = S$ where S is the entropy, and $\left(\frac{\partial G}{\partial P}\right)_T = V$ where V is the volume

Therefore $\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{L}{T\Delta V}$ where L is the latent heat (enthalpy change) for the phase change. This is the Clausius-Clapeyron equation. At a triple point, the Gibbs free energies of the three phases (G_1, G_2, G_3) must be equal and the entropy and enthalpy (latent heat) changes for all three phase changes ($1 \longrightarrow 2$, $2 \longrightarrow 3$, $1 \longrightarrow 3$) at that point may be calculated, given the pressure, temperature ($\frac{dP}{dT}$) and volume changes. [Back]

[f] The phase diagram for heavy water (D_2O) differs little from the diagram for H_2O given the scales used in the diagram. A more accurate representation would be by shifting the temperature scale by about 3.6 K as most of the triple points for D_2O are 3 - 4 K warmer than those for H_2O (see above). The pressure differences are positive or negative but not significant given the logarithmic scale used. [Back]

Source:http://www1.lsbu.ac.uk/water/phase.html